NEW PATHWAYS IN LASER INDUCED THERMAL GAS-PHASE CHEMISTRY

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ABSTRACT   Various cw CO_2 laser-induced reactions in the presence of energy conveying SF_6 are shown to proceed in a specific way due to the absence of heterogeneous stages that are very difficult to avoid in normal hot wall reactors. Truly homogeneous courses are reported for some dehydrochlorinations, oxidations of perhaloalkenes with molecular oxygen, and decomposition of representatives of amines, nitroalkanes and perfluorinated, bridged and unsaturated derivatives of carboxylic acids.
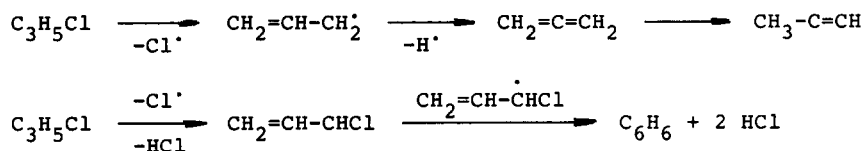
INTRODUCTION

Thermal chemistry of organic and organometallic compounds shows many examples of reactions that are dramatically influenced by heterogeneous contributions from hot reactor surface. These steps are sometimes very difficult to avoid and true homogeneous mechanisms remain hidden from the observer. From among many techniques earlier designed to minimize surface effects, the laser heating of limited gas--phase volume far from cold reactor surface seems most reliable. The technique of continuous-wave CO_2 laser induced gas phase reactions in the presence of energy conveying sulfur hexafluoride |1|, which is sufficiently stable and an excellent absorber of CO_2 laser radiation, enables to run chemical reactions homogeneously and reveals truly homogeneous mechanisms and reaction products even at high conversions.

This article gives a brief overview of cw CO_2 laser induced reactions investigated in our laboratory and shows the importance of the laser technique in proper understanding of some dehydrochlorinations, oxidations of alkenes with molecular oxygen, thermolysis of representatives of alkylamines, nitroalkanes and cyclic compounds and decarbonylations of some carboxylic acids and their derivatives.

Dehydrochlorination

Conventional dehydrochlorination of some unsaturated halides is accompanied by decomposition reactions of primary products of which the decomposition of allyl chloride is an example. This reaction leads to complex mixtures of gaseous products, hexa-1,5-diene, cyclohexa-1,3-diene, benzene and others. Laser induced process is consistent with substantially simplified reaction scheme

$$C_3H_5Cl \xrightarrow[-Cl^\bullet]{} CH_2{=}CH{-}CH_2^\bullet \xrightarrow[-H^\bullet]{} CH_2{=}C{=}CH_2 \xrightarrow{\hspace{1cm}} CH_3{-}C{\equiv}CH$$

$$C_3H_5Cl \xrightarrow[-HCl]{-Cl^\bullet} CH_2{=}CH{-}CHCl \xrightarrow{CH_2{=}CH{-}\overset{\bullet}{C}HCl} C_6H_6 + 2\ HCl$$

and leads to the formation only of propyne, propadiene and benzene with total yield of the C_3H_4 compounds three times higher than in conventional process [2].

Polychlorinated alkanes and alkenes can eliminate hydrogen chloride to form corresponding alkenes or alkynes and the mechanism of this dehydrochlorination is a blend of molecular and radical-chain process. The latter is considered a draw-back for the reaction to be utilized on a laboratory-scale for preparation of ole-fins, but an effort to remove radical-chains had not met success.

Laser induced reactions of 1,2-dichloroethane, 1,1-dichloroethane, 1,1,1-tri-chloroethane, cis- and trans-1,2-dichloroethene and trichloroethene [3,4] are very clean and proceed without formation of secondary products. They are not influenced by an addition of propene and chloroethane that are known a radical-chain retarder and chlorine atom scavenger. The absence of the effect of these probing agents on total reaction rate of dehydrochlorination as well as the total rate constants for laser-induced dehydrochlorination of chloroethane in the presence of the polychlo-rinated alkanes or alkenes (Table 1) are consistent with purely molecular mecha-

Table 1   Rate constants, k for the laser-induced dehydrochlorination of chloroet-hane in the presence of chlorinated hydrocarbon[a]

Chlorinated hydrocarbon	Laser output W	$10^3 \cdot k$ s^{-1}
-	5	4.21
1,2-dichloroethane	5	4.56
1,1,1-trichloroethane	5	4.49
cis- and trans-1,2-dichloroethene	5	4.15
trichloroethene	5	4.94
-	9	13.8
chloroform (2.1 kPa)	9	25.0
chloroform (3.5 kPa)	9	40.0
1,2-dichloroethane	9	17.5

[a]In the chlorinated hydrocarbon-SF_6-argon-chloroethane system

nism of the laser induced dehydrochlorination. Care has to be however taken to use lower laser output, since radical chains become important with higher value of this parameter. An increased reaction rate for chloroethane decomposition in the presence of chloroform decomposing only through the liberation of chlorine atoms and in the presence of 1,2-dichloroethane (Table 1) along with the observation of inhibiting effect of propene at higher laser powers during dehydrochlorination of chloroalkanes [5] are supportive of this view. These results point out the impor-tance of hot walls for the initiation of radical-chain dehydrochlorination.

Oxidation of halogenated alkenes

The oxidation of perhalogenoalkenes with molecular oxygen is normally a very complex reaction involving the attack of molecular oxygen on alkene molecules, carbenes or energized alkene-O adducts and it yields a number of products as per-fluorocyclopropanes, carbonyl halides, alkene oxides and also peroxydic polymers. The reaction scheme for the oxidation of tetrafluoroethane can be depicted as fol-lows.
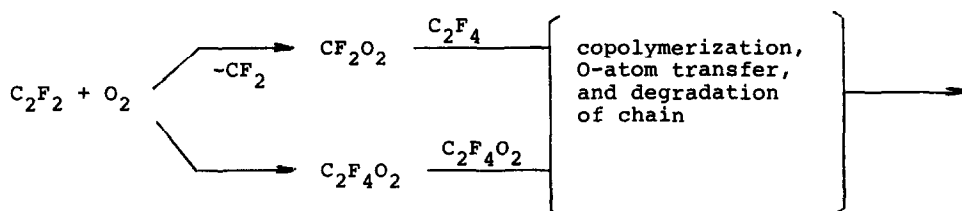
The laser driven oxidation of C_2F_4 |6,7| is accompanied with luminescence and its intensity correlates with the reaction rate. It is remarkable that this reaction yields only carbonyl fluoride regardless whether conversion is low or complete. No effect on the reaction rate of triethylamine, which is currently considered a most efficient quencher of singlet $O_2(^1\Delta)$ oxygen, and no effect of propene, which retards radical-chain processes, show that the laser-driven oxidation involves non-chain reaction of molecular oxygen in its triplet $O_2(^3\Sigma)$ state. By using cyclization of hexafluoro-1,3-butadiene to hexafluorocyclobutene as a marker, it was possible to obtain an activation energy of $E_a = 241$ kJ.mol^{-1}. The total rates at the estimated temperatures are fairly low to admit that the oxidation proceeds via the sequence $C_2F_4 \longrightarrow 2$ CF_2, $CF_2 + O_2 \longrightarrow COF_2 + O$. Chemiluminescence spectra were interpreted as $S_1 \longrightarrow S_0$ and $T_1 \longrightarrow S_0$ transitions of electronically excited COF_2 and all the facts are in agreement with a new mechanism involving intermediary dioxetane and its cleavage:
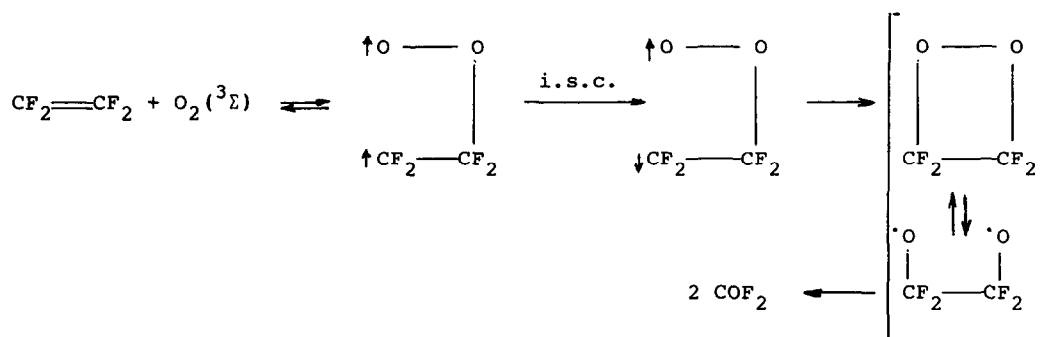
This mechanism was also used for the explanation of time resolved emission spectra of the TEA CO_2 laser photosensitized oxidation of tetrafluoroethene and decafluorocyclopentane |8|, and for cw CO_2 laser photosensitized oxidation of hexafluoropropene, chlorotrifluoroethene, 1,1-dichlorodifluoroethene, 1,2-dichlorodifluoroethene and hexafluoro-1,3-butadiene |9|. The effective temperatures of the laser-thermalized olefin-SF_6-O_2 systems were estimated between 600-700 K. Under these conditions neither O atoms should be generated, nor primary excitation of the olefin should occur. The alternative possible chanel $^1CF_2 + ^3O_2 \longrightarrow$ is in fact too slow to compete with the carbene reassociation and the rate constant of the later exceeds up to 1000 K that of the former by at least 2 orders of magnitude. The operation of the carbene mechanism also implies that during the oxidation of unsymmetrical olefin two new symmetrical olefins should be formed, which was not observed. Hence, the similar dioxetane mechanism should be operative:
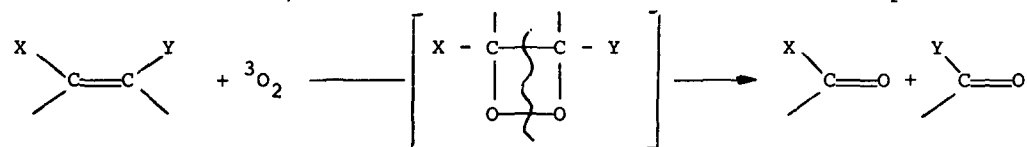

Relative reactivities of the individual olefines at $T_{eff} = 710$ K are very alike (1.0 - 1.1) and they apparently reflect similar rates of $^3O_2$ addition across

double bond.

Thermolysis of tert.-butylamine

Complexity of conventional thermolysis of amines precludes to use this reaction for generation of amino radicals. Tert.-butylamine had been believed to decompose by two independent first-order processes

$$(CH_3)_3C-NH_2 \nearrow (CH_3)_2C=CH_2 + NH_3$$
$$\searrow (CH_3)_2C=NH + CH_4$$
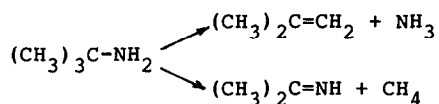
with very similar activation energies. This means that the ratio between the products formed by these processes does not significantly vary with reaction temperature and that the cleavage of the C-C and C-N bonds at different temperatures takes place with equal probability.

The laser-driven decomposition of tert.-butylamine |10| differs remarkably from conventional thermolysis in the ratio of methane and isobutene produced. The value is not constant, but depends on the decomposition conditions and reaction progress (Fig. 1).
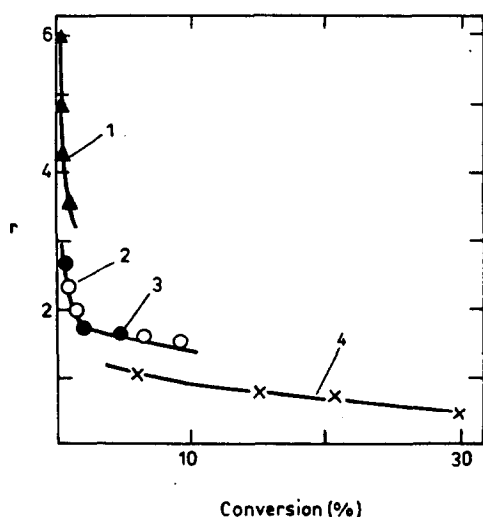

Fig. 1
Dependence of the molar isobutene:
:methane ratio, r, upon the reaction progress. Curves 1-4 relate to increasing effective temperature

Conversion (%)

Moreover, this reaction shows preference for the C-N bond cleavage and its course can be only explained by assuming that the C-N cleavage is reversible. The laser--driven reaction between isobutene and ammonia was actually observed and it is, to our knowledge, the first example of ammonia uncatalysed addition to olefin. The only change upon the irradiation of $NH_3-C_4H_8-SF_6$ mixture is a decrease in isobutene and increase in methane concentration, which implies that the addition of ammonia to isobutene initially yields tert.-butylamine which then decomposes to methane and unstable 2-propaneimine. The new mechanism of the laser-induced decomposition was verified by simulation of kinetic curves.

Thermolysis of 2-nitropropane

This reaction is reported as proceeding via two competitive processes, namely HONO molecular elimination and C-N bond fission to form propene and nitrous acid, followed by a series of secondary reactions initiated by the attack of the decomposition products of nitrous acid on the parent molecule. The secondary steps were inferred to occur heterogeneously, but the reaction was not elluciated comple-

tely.

The laser irradiation of $C_3H_7NO_2$-SF_6 (inert gas) mixtures |11| yields propene, nitrogen oxides, water and methane. The computed temperature profiles (Fig. 2) and estimated effective temperatures using ethylacetate decomposition as a marker (Table 2), support the view that true homogeneous decomposition of 2-nitropropane at effective temperatures 700-1000 K involves C-N bond fission and implies thus that the five center molecular elimination of HONO is preferred either at lower temperatures or facilitated by the surface.

Table 2   Mean effective temperatures for different modes of 2-nitropropane decomposition

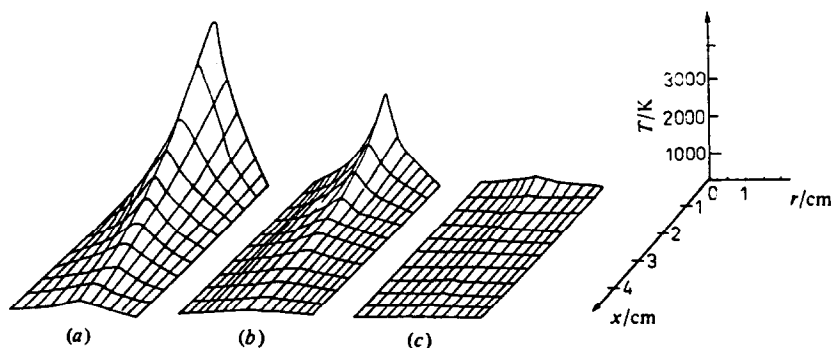| Mode	T / K	
	2 NP + SF$_6$	2 NP + SF$_6$ + Ar
partly heterogeneous	910	1000
five center molecular elimination of HONO	760	840
C-N bond fission	710	680

Fig. 2   Temperature distributions for computed for SF$_6$ (a), SF$_6$ + argon (b), and SF$_6$ + helium (c)

Thermolysis and spirohexane

Thermal decomposition of three-membered rings has been predicted to give ethylene and carbenes, but both cyclopropane and spiropentane derivatives cleave via diradicals into propenes or methylenecyclobutanes, which can be suspected to be brought about by a surface involvement.

The cw CO_2 laser-induced decomposition of spirohexane |12| yields ethylene, 1,3-butadiene and methylenecyclopropane as final products and the mechanism of this reaction is given in a scheme below.
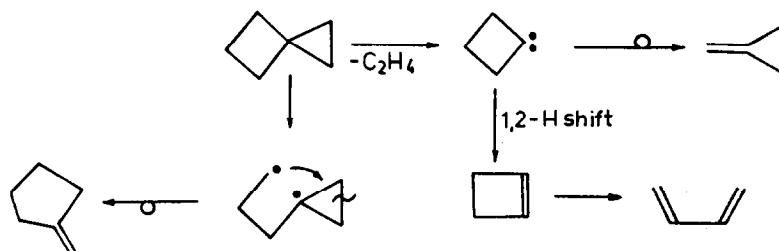
The reaction thus represents the first example of the cleavage of the three mem-
bered ring into carbene and ethylene where these products are the major ones!

The temperature dependence of the rate coefficient (log $A = 15.1$ s^{-1}, E_a =
= 243 kJ.mol^{-1}) is very similar to that for the cleavage of the three-membered
spiropentane and appears to indicate cleavage of the three-membered ring of spiro-
hexane as the rate determining process. The intermediacy of the cyclobutylidene
as a precursor of both methylenecyclopropane and cyclobutene gets kinetic support
from the almost constant methylenecyclopropane : 1,3-butadiene ratio at different
reaction progress (Table 3).

Table 3   Representative methylenecyclopropane:1,3-butadiene ratios

Laser output W,	Conversion, %	Ratio
5	7.3	0.20
	9.5	0.35
	22.4	0.30
8	34.3	0.28
	42.7	0.26
	87.9	0.27

Surprising difference in behaviour of intermediary diradicals postulated in the
decomposition of both spirohexane and spiropentane, namely

and
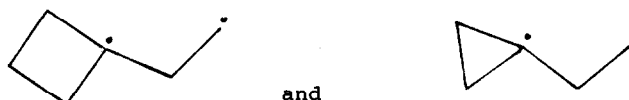
can be associated with a higher stability of cyclobutylidene compared to cyclo-
propylidene and we continue study of laser driven decompositions of spiro|2.n|al-
kanes and their deuteriated analogues to find out whether the suggested mechanism
is correct.

Thermolysis of silicon-containing cyclic compounds

Thermal fragmentation of silacyclobutanes $R_2\overline{SiCH_2CH_2CH_2}$ was intensively studied
due to its capability to yield reactive silaethenes. Normally these transient spe-
cies undergo mostly cyclodimerization.

Laser-driven decomposition of 1-methyl-1-silacyclobutane |13| and 4-silaspiro-
|3.4|octane |14| remarkably differs in that it is a very selective way for pro-
duction of new organosilicon polymers. The mechanism of these reactions can be
depicted as
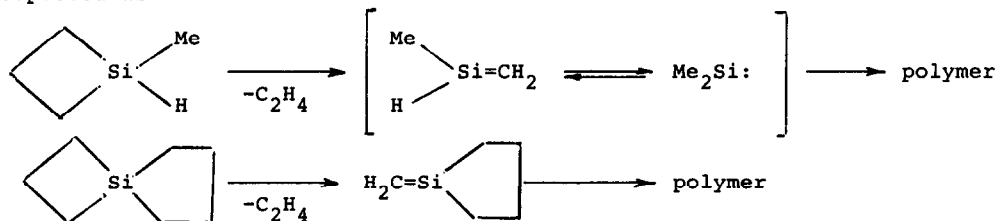
The polymers are deposited at the reactor surface and the reaction can be used
for modification of thermally unstable surfaces.

Thermolysis of isobornyl acetate

The gas-phase thermolysis of alkyl esters without β-hydrogen and of esters with cyclic, bridged or spiro structure occurs with (at least some) rearrangement which was explained by means of ionic intermediates. Many examples relate to reaction conditions that make surface catalysis possible and it is therefore not clear whether rearrangements proceed in the gas phase or whether they are surface-assisted. It has been postulated that the transition state achieved in the gas phase is less ionic than in solution and that neighboring assistance or migration to the reaction center is enhanced with the development of charge at both centers. The stabilization of such polar transition state on a surface can be a driving force for the rearrangement to occur. We have addressed this problem by studying the laser driven thermolysis of isobornyl acetate |15|. Normal decomposition affords a mixture of bornylene, tricyclene and camphene, the former being a normal product of cis-1,2-elimination and the latter the rearranged products explained in terms of a synartetic assistance from proximal positions.

Laser-irradiation of isobornyl acetate-SF$_6$-marker-argon mixtures gives ethylene, trimethylcyclopentadienes, toluene, bornylene, tricyclene, camphene and some small quantities of unidentified products. The reaction was treated kinetically with a marker (decomposition of cyclohexyl acetate) and its course is given in scheme below.
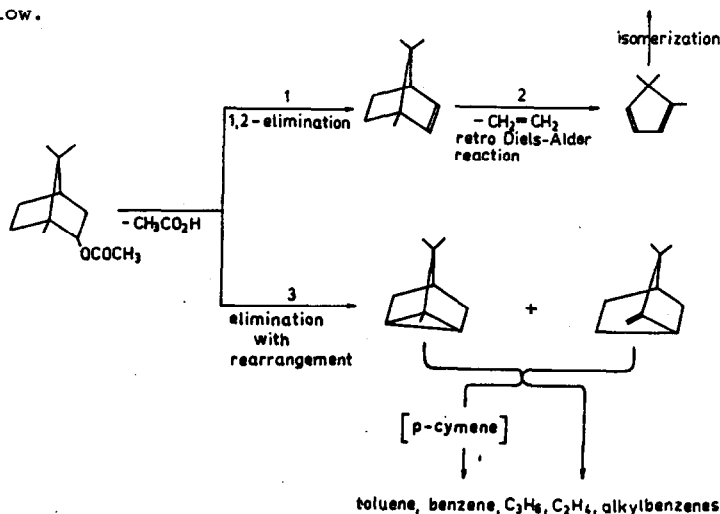
In order to determine the relative importance of cis-1,2-elimination and elimination accompanied by rearrangement the reaction scheme can be written as
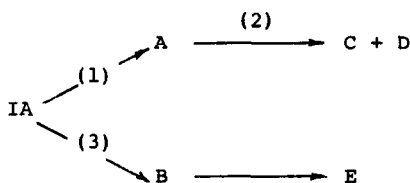
where A, C, D, B and E designate, in the given order, bornylene, trimethylcyclopentadiene, ethylene, tricyclene + camphene, and the products yielded by camphene and tricyclene. The calculated rate constants at some T_{eff} are summarised in Table 4.

It appears that bornylene decomposes, within the temperature range studied, more than an order of magnitude faster than it is formed. The data definitely show that the rearranged products are formed in the gas-phase without any parti-

Table 4 Rate constants k, k_1, k_2 and k_3 at some mean effective temperatures T_{eff}

| T_{eff} (K)	Rate constant (error $\pm$ 5 %) (s^{-1})			
	k	k_1	k_2	k_3
610	4.1×10^{-4}	2.8×10^{-4}	5.1×10^{-3}	1.3×10^{-4}
639	2.5×10^{-3}	1.9×10^{-3}	2.6×10^{-2}	6.1×10^{-4}
646	5.0×10^{-3}	1.3×10^{-3}		3.6×10^{-3}
662	1.0×10^{-2}	3.9×10^{-3}	2.8×10^{-1}	6.4×10^{-3}

cipation of stabilizing interaction from reactor surface. A certain approximation, i.e. the common treatment of both rearrangements as the Arrhenius plot ln k_3 vs. T_{eff}^{-1} leads to log A $\sim$ 19 s^{-1} and E_a $\sim$ 270 kJ.mol^{-1}. These values can be compared to those for clean cis-1,2-elimination (log A $\sim$ 10 s^{-1}, E_a = 170 kJ.mol^{-1}, and are in accord with the expected looser and also more ionic transition state for the formation of rearranged products, since it is known that more ionic transition states in the gas-phase unimolecular reactions imply a less synchronized cleavage and thus demand a higher activation energy.

Decarbonylation of some carboxylic acid derivatives

Decarboxylation and decarbonylation are the dominant and competing processes during thermal decomposition of carbocyclic acids and their derivatives. The decomposition of perfluorinated compounds containing carboxyl group is rather sensitive to the reactor material, but there are no strong indications of such an effect in the decomposition of esters.

Conventional thermolysis of perfluorinated acetic acid yields carbon dioxide, difluoromethyl trifluoroacetate, carbon monoxide, trifluoroacetyl fluoride, carbonyl fluoride and trifluoromethane, and thermolysis of trifluoroacetic acid anhydride affords carbon monoxide, carbon dioxide and trifluoroacetyl fluoride. These compounds were explained by a mechanism with the initial step

$$CF_3COX \longrightarrow CF_3COF + {}^{\cdot}CF_2CO_2^{\cdot}$$
$$(X = OH \text{ or } OC(O)CF_3)$$
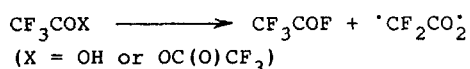
and the following heterogeneous reaction of the biradical on the reactor walls:

$$^{\cdot}CF_2CO_2^{\cdot} \longrightarrow :CF_2 + CO_2$$
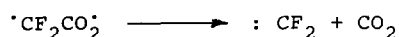
Laser-driven decomposition of both compounds |16,17| occurs in a different way and results in the formation of mostly carbonyl fluoride and carbon monoxide. It was tempting to conclude that different mode of the decomposition of intermediary diradical can be the explanation:
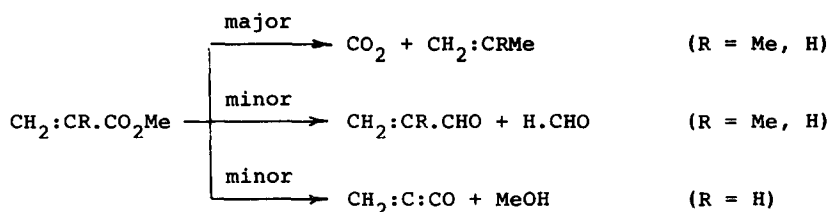
$$^{\cdot}CF_2CO_2^{\cdot} \longrightarrow COF_2 + CO \quad (\text{major, A})$$
$$\longrightarrow CO_2 + :CF_2 (\text{minor, B})$$
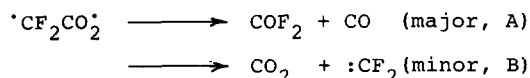
The higher preference of the channel A over B at lower SF$_6$ pressures (and larger reaction zone with perhaps lower temperature) is not consonant with the suggestion that both A and B chanels start from a common energetical point. It is therefore possible that $^{\cdot}CF_2CO_2^{\cdot}$ species follows channel A or B depending upon the amount of energy available.

Thermolysis of esters having unsaturation immediately adjacent to the -CO$_2$- grouping is known to proceed via competing decarboxylation, acyl-oxygen and alkyl-

-oxygen scissions. With methyl acrylate (MA) and methyl methacrylate (MMA) the decarboxylation pathway predominates:

major
$\longrightarrow$ CO$_2$ + CH$_2$:CRMe   (R = Me, H)

minor
CH$_2$:CR.CO$_2$Me $\longrightarrow$ CH$_2$:CR.CHO + H.CHO   (R = Me, H)

minor
$\longrightarrow$ CH$_2$:C:CO + MeOH   (R = H)

The irradiation of MA-SF$_6$ and MMA-SF$_6$ mixtures with cw CO$_2$ laser |18| yields products shown in Fig. 3 and Table 5.
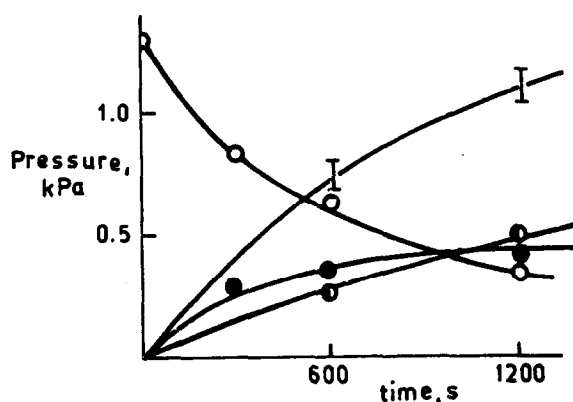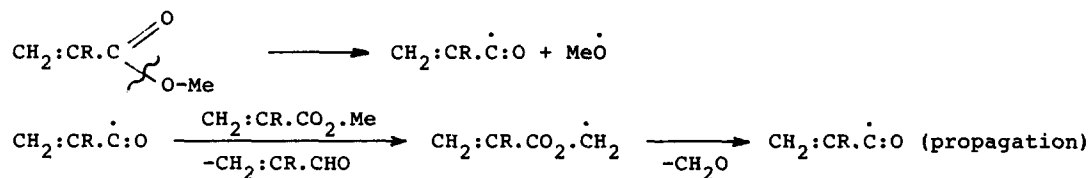

Fig. 3   Reaction progress of the laser powered (10 W) decomposition of MA in MA-
         -SF$_6$ (both 1.3 kPa) mixture
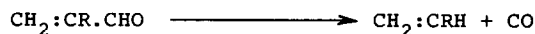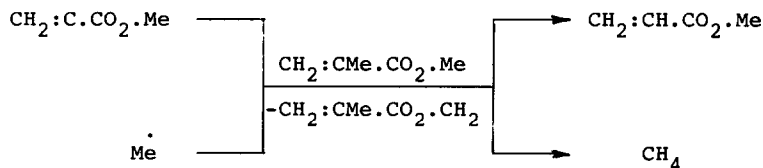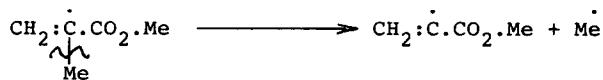   MA (O), CH$_2$:CH.CHO (●), C$_2$H$_4$ (◑), CO (⊥)

Table 5   Laser powered decomposition of methyl methacrylate

SF$_6$ (mol %)	Total pressure	Conversion %	Products (kPa)							
			acro-lein	C$_3$H$_6$	CO	C$_2$H$_4$	CH$_4$	C$_2$H$_2$	C$_4$H$_8$	MA
35	3.1	61	0.20	0.80	0.8--0.9	0.10	0.10	0.02	0.01	0.01
55	2.7	68	0.09	0.50	0.5--0.7	0.10	0.10	0.04	0.01	0.01

The laser induced decompositions differ remarkably from conventional pyrolysis in that they do not yield carbon dioxide. Homogeneous decompositions of MA and MMA are dominated by acyl-oxygen scission and can be described by a mechanism involving radical chains:

Major channel (R = H, Me)

CH$_2$:CR.C $\overset{O}{\underset{O-Me}{\diagup}}$ $\longrightarrow$ CH$_2$:CR.Ċ:O + MeȮ

CH$_2$:CR.Ċ:O $\xrightarrow[-CH_2:CR.CHO]{CH_2:CR.CO_2.Me}$ CH$_2$:CR.CO$_2$.ĊH$_2$ $\xrightarrow[-CH_2O]{}$ CH$_2$:CR.Ċ:O (propagation)

$$CH_2{:}CR.CHO \longrightarrow CH_2{:}CRH + CO$$

Minor channel

$$CH_2{:}\overset{.}{C}.CO_2.Me \longrightarrow CH_2{:}\overset{.}{C}.CO_2.Me + \overset{.}{Me}$$
$$\underset{Me}{}$$

$$CH_2{:}C.CO_2.Me \longrightarrow$$
$$CH_2{:}CMe.CO_2.Me \longrightarrow CH_2{:}CH.CO_2.Me$$
$$-CH_2{:}CMe.CO_2.CH_2$$
$$\overset{.}{Me} \longrightarrow CH_4$$

These chains were proved by observing inhibition in the presence of propene and cyclohexene. Retro-Diels-Alder reaction of cyclohexene used as a marker revealed that data of the log k_{total} vs. T_{eff}^{-1} plot for MA and MMA decompositions can be fitted with a common line and lead to E_a = 316 kJ.mol^{-1} and log A = 18.8 s^{-1} which are very close to the accepted values for simple fission of molecules into two radicals and appear thus to be associated with the initial acyl-oxygen cleavage.

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